

A HIGH-TEMPERATURE METHANATION CATALYST FOR SNG APPLICATIONS

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INTRODUCTION

The political and economic background to the development of coal-based Substitute Natural Gas processes will be familiar to readers and, therefore, need not be detailed herein. The technical problem can be regarded very simply as having two parts, namely the gasification of coal followed by conversion of the product gas into SNG. Proven commercial processes, eg Koppers-Totzek, Lurgi, etc exist for coal gasification and several second generation processes are in various stages of development in the United States and elsewhere. The compositions of gases produced by these processes differ depending upon operating conditions ie pressure, temperature, steam addition, etc. In general, however, dry gas compositions are typically in the range:

CO ₂	0 - 30%
CO	10 - 60%
H ₂	25 - 75%
CH ₄	0 - 20%

Alternative methods of upgrading such a gas to pipeline quality exist, the major problem being to combine the degree of, highly exothermic, methanation required with a low final exit temperature compatible with favourable thermodynamic equilibrium for methane formation. A process incorporating a high recycle ratio of product gas back through the methanator has been described (1) as a means of moderating the temperature rise in the methanator. A more elegant and economic solution, however, is a straight-through process using a series of methanators operating at successively lower exit temperatures (2,3). The viability of such a scheme depends upon the availability of a methanation catalyst, or catalysts, capable of operating under the design conditions for commercially acceptable periods. The purpose of the work described in this paper was to develop and demonstrate such a catalyst. This work comprised part of a collaborative agreement between ICI and Krupp-Koppers GmbH to develop processes for the production of SNG from coal based upon the Koppers-Totzek coal gasification process.

EXPERIMENTAL

Process Design

The basic philosophy during this programme was to take a "typical" gas composition, to subject it to the type of methanation process necessary to produce SNG and to evaluate the performance of various catalysts, commercially proven and experimental, in the duties involved. The gas composition selected appears in Table 1 (column 1) and will be seen to have H₂ + CO = 74% (dry basis). While not referring specifically to a particular gasification process, this is representative of the composition of gas to be methanated. In fact, the virtual absence of methane from the original gas increases the demand on the methanation section in comparison with processes in which the incoming gas already contains a significant proportion of methane.

Table 1

Gas Compositions and Temperatures in Methanation Process

Position	1	2	3	4	5	6
CO	31.14	14.47	14.47	4.29	4.29	0.34
CO ₂	24.66	40.15	40.15	53.93	53.93	62.70
H ₂	42.91	35.50	35.50	20.26	20.26	5.83
CH ₄	0.08	8.52	8.52	19.84	19.84	29.13
N ₂ + Ar	1.21	1.36	1.36	1.68	1.68	2.00
	100.00	100.00	100.00	100.00	100.00	100.00
H ₂ O	67.3	72.3	72.3	94.4	94.4	118.2
T°C	398	729	325	590	300	428

The process design studied is illustrated in Figure 1, the gas composition and temperature at each stage appearing in Table 1. Incoming gas is mixed with steam (67.3 vols : 100 vols dry gas) and preheated to approximately 400°C at the inlet to the first methanator. Operating pressure is 30 atms (425 psig). The gas leaves the methanator at an adiabatic equilibrium temperature of approximately 730°C, is cooled to 325°C by raising high pressure steam in a boiler and passes to the second methanator. Further methanation occurs and the gas leaves at the adiabatic equilibrium temperature of 590°C. It is again cooled, by raising steam, to 300°C and passes to the final "wet" methanator where it attains an adiabatic equilibrium temperature of about 430°C. At this stage, the gas has a methane content (dry basis) of approximately 29% (78% after CO₂ removal). Subsequent processing stages would include water removal, final "dry" methanation and CO₂ removal to produce the final SNG. Design constraints were incorporated on nickel carbonyl formation in the reactors, which defined the minimum inlet temperatures possible to the first two methanators, and on the amount of steam added which was used to control the maximum temperature in the first methanator below 750°C. Neither the latter, nor the inlet to the third methanator which was arbitrarily set at 300°C, has been rigorously optimised so some flexibility in these values exists.

Catalyst Evaluation

Our previous experience in development and use of catalysts for naphtha- and methane-steam reforming as well as for methanation processes meant that, at the outset of this work, we had "on the shelf" a number of catalysts expected to have activity for the reactions of interest. A laboratory screening test was therefore set up, operating at atmospheric pressure, by which the initial activity of these catalysts could be evaluated rapidly under appropriate conditions of temperature and gas composition. This permitted selection of catalysts for further testing in semi-technical reactors operating under simulated process conditions. Previous experience suggested that provision of a catalyst suitable for the third methanator would present no difficulty so attention was concentrated on the preceding two. In general, steam reforming catalysts were found to lose their low temperature activity relatively rapidly while commercial methanation catalysts were unstable at high temperatures (>600°C). However, with experimental preparations it was soon found that low temperature activity was no problem. This allowed evaluations to be performed under first methanator conditions, with the expectation that comparative results would also be valid under second methanator conditions. Numerous catalyst lifetests, of durations varying between one and seventy days, were carried out under these conditions.

In summary, the outcome of the first phase of the catalyst evaluation and development programme was the production of a new high-nickel, co-precipitated formulation (NiO approx 60% loss free) which appeared to have the necessary activity, stability and physical strength for the applications envisaged. When a preferred catalyst formulation had been selected, its preparation was scaled up from the laboratory to a pilot plant located at our catalyst manufacturing site in Clitheroe, Lancashire. This unit is a reduced-scale simulation of a commercial production unit and its use is an essential stage in the development of a procedure for manufacture of a commercial catalyst. Its normal batch size is 15-20 kg and the catalyst manufactured therein was used for all subsequent testing. To demonstrate its properties, three semi-technical reactors were linked in series to permit a long lifetest with the catalyst operating under the conditions of the three methanators.

In common with other nickel-based catalysts, this formulation is susceptible to poisoning by sulphur compounds in the process gas stream. The extent of this was therefore minimised by incorporation of a vessel of desulphurisation catalyst (zinc oxide, ICI catalyst 32-4), upstream of the point of steam addition, running with maximum temperature 250-300°C. By this means, the sulphur level in the process gas was reduced below 0.1 mg S/Nm³ (dry basis), see below.

The semi-technical reactors used were fabricated from 18/8 Ti stainless steel tube, nominal 1 inch id, overall length 30 ins. The catalyst bed, 12 ins deep, was arranged centrally in the reactor which was also fitted with an internal thermocouple sheath containing six equally-spaced thermocouples positioned throughout the catalyst bed. The reactors were fitted with two external electrical heaters, the first to permit attainment of the selected bed inlet temperature and the second adiabatically controlled to compensate for heat losses. The whole assembly was then surrounded by several inches of inert insulation material. Figure 2 is a simplified illustration of one reactor assembly.

For the performance tests, each reactor was loaded with an undiluted bed, volume 135 ml, of catalyst in the form of pellets diameter 5.4 mm, height 3.6 mm. This was reduced to the active form by passage of pure, dry hydrogen for several hours at 450-500°C and space velocity about 25,000 hr⁻¹. Because these reduction conditions were easily obtained in our equipment, no specific study was made of the reducibility of this catalyst although it has been shown that effectively complete reduction is obtained by passage of hydrogen for two hours at 300°C. After the reduction period, the inlet temperature of each reactor was adjusted to the design setting and the appropriate rate of water fed to the vaporiser upstream of the first methanator. After a few minutes, the hydrogen was replaced by pre-mixed process gas at a flow-rate corresponding to a dry gas space velocity of 10,000 hr⁻¹ relative to the catalyst volume in the first methanator. Reduction in dry gas volume through the methanators made the effective (dry) space velocity through the second and third reactors 8865 hr⁻¹ and 7160 hr⁻¹ respectively. Methanation began immediately and steady state conditions in all three reactors were reached within a few hours. The tests were then allowed to run under constant conditions for a prolonged period, catalyst performance being monitored by regular measurement of the temperature profile in each catalyst bed. Outlet gas compositions, which corresponded to the equilibrium composition at each outlet temperature, were monitored by an on-line gas chromatograph.

Figures 3, 4 and 5 show the temperature profiles in each bed at the start of these tests and after continuous operation for the periods indicated. The test ran without significant disturbance for 1500 hrs at which time a plant failure caused an interruption to the water supply and consequently massive carbon deposition in all three reactors. After this upset, it proved impossible to restart the second and third methanators so these were discharged and the catalyst submitted to post-mortem examination. The first methanator was restarted although the temperature profile was found to be displaced substantially down the catalyst bed. Within a few days, however, it recovered to almost its original position (see Figure 3) and then remained stationary until 2200 hrs at

which time the test was terminated.

Post-mortem examination of the catalyst discharged from several levels in each bed revealed that it had mean nickel crystallite sizes in the ranges 750-1000Å, 270-400Å and 160-190Å for the first, second and third methanators respectively. Considering the duration and operating conditions of these tests, this crystallite growth, from an original size of about 100Å, demonstrated the inherent stability towards sintering of this catalyst formulation. Further, the excellent performance during the lifetests showed that this degree of sintering had had no detrimental effect on catalyst activity under the relevant operating conditions. The inference to be drawn is that, with a catalyst of high active metal content operating in a relatively high temperature range, some crystallite growth can be tolerated. The small amount of growth of the catalyst in the second methanator which had run up to 590°C was particularly noteworthy. The results reported were obtained before a full catalyst composition optimisation was carried out. Therefore, although it is not required for these duties, we would expect to be able to design a catalyst with greater resistance to sintering if necessary.

Discharged catalyst from the first two methanators was found to contain sulphur corresponding to an absorption of about 0.015 mg S/Nm³ of gas passed in the first reactor followed by about 0.065 mg S/Nm³ in the second, ie a total concentration of 0.08 mg/Nm³ in the process gas inlet to the first reactor. This concentration caused no significant deactivation of the catalyst in the first bed and a deactivation rate of 1.0-1.5 inches per 1000 hrs in the second which, it is reasonable to postulate, would have been lower at a lower inlet sulphur level. This could have been obtained by optimising the desulphurisation catalyst operating conditions but, in view of the length of test which would have been required to demonstrate an improvement over the performance already observed, this was not felt to be a worthwhile exercise. It will be seen that the distribution of sulphur between the two beds was as would be expected for their inlet and outlet temperatures and the known fact that formation of nickel sulphide is thermodynamically favoured at low temperatures.

DISCUSSION

The catalyst lifetests described above have demonstrated that a formulation has been developed with the activity and stability needed to methanate a variety of process gases at temperatures up to 750°C. By proving the catalyst under simulated process conditions in tests of 2-3 months duration we have been able to show that its rate of deactivation is low enough to be commercially acceptable. Further, by testing under "typical" coal gas methanation conditions, we have acquired the confidence to predict that this catalyst will also perform satisfactorily under the variety of conditions encountered in different proposed coal gas methanation processes. The high temperature capability of this catalyst has the particular advantage of permitting the use of a straight-through methanation system without the need for recycle of product gas for temperature control.

The applicability of this catalyst to processes other than coal gas methanation should also be noted. For example, high temperature methanation steps may be used as sources of heat for steam generation. In such a system, methanatable gas is produced in an endothermic methane-steam reforming stage, piped to the site where the steam is to be generated, methanated, cooled in boilers and feed water heaters, then piped back to the steam reforming stage (4). To use such a process optimally, it is clearly necessary for the methanation catalyst to function over as large a temperature range as possible.

REFERENCES

- 1 K.H. Eisenlohr, F.W. Moeller and M. Dry in "Methanation of Synthesis Gas," Advances in Chemistry Series 146, 1975, p 113.
- 2 J.E. Franzen and E.K. Goeke, paper presented at Sixth Synthetic Pipeline Gas Symposium, Chicago, Illinois, October 1974.
- 3 G.A. White, T.R. Roszkowski and D.W. Stanbridge in "Methanation of Synthesis Gas," Advances in Chemistry Series 146, 1975, p 138.
- 4 General Electric Co., U.S. patent application no 484802, German OLS 2528660.

FIGURE 1. METHANATION PROCESS

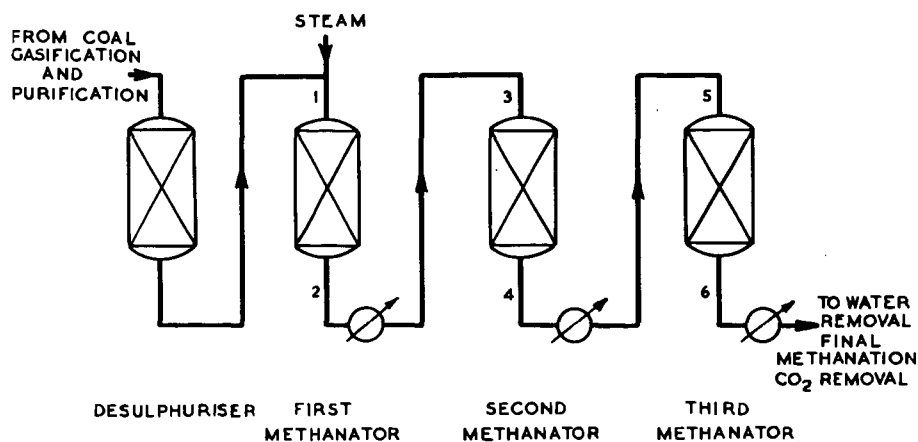


FIGURE 2. METHANATION SEMI-TECHNICAL PLANT REACTOR ARRANGEMENT (SIMPLIFIED)

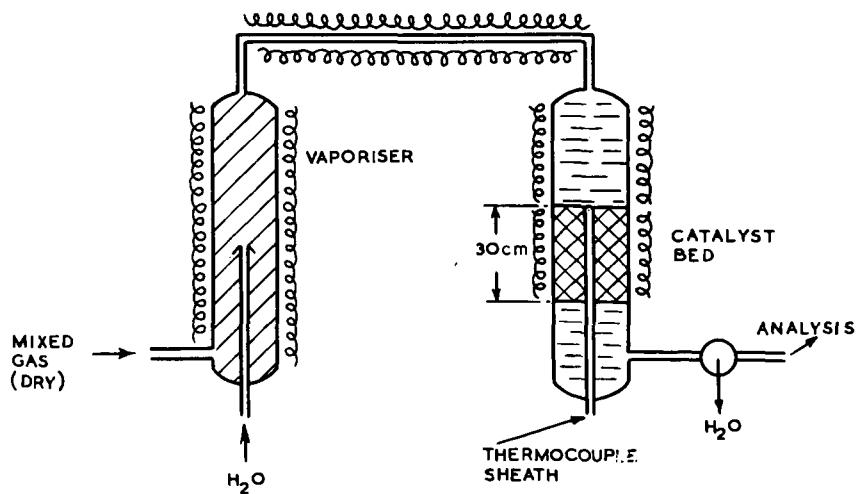


FIGURE 3. FIRST METHANATOR TEMPERATURE PROFILE

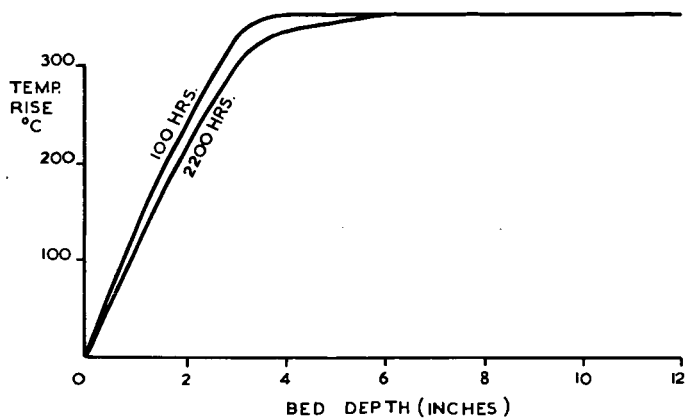


FIGURE 4. SECOND METHANATOR TEMPERATURE PROFILE

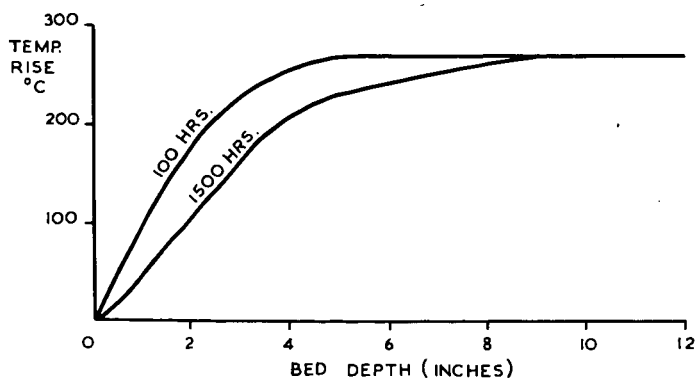


FIGURE 5. THIRD METHANATOR TEMPERATURE PROFILE

